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奈米微晶鑽石薄膜製程及其應用於場發射電子源之研究

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奈米微晶鑽石薄膜製程及其應用於場發射電子源之研究

計畫編號：92-2216-E-032-006
主持人： 林諭男
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摘要：

本研究探討 CH_4/H_2 氣體比及偏壓電場對奈米微晶鑽石孕核行為之影響。研究發現 SEM 微結構與拉曼晶體結構受上述製程參數之影響不大，但是電子場發射特性則深受其影響。相信最重要之影響因素是在奈米微晶鑽石晶粒微小化之同時，具有 sp^2 鍵結之晶界比例提高的效果。

Abstract

Effects of CH_4/H_2 ratio and bias voltage on the nucleation behavior and the characteristics of the nano-diamonds were investigated. Among the two major factors, the bias-voltage shows more prominent effect on modifying the nucleation rate for diamond nuclei and granular structure for the nano-diamonds. While the SEM microstructure and Raman crystal structure of the films insignificantly vary, the electron field emission properties of the materials markedly change, with these deposition parameters. The main factor modifying the electron field emission properties is assumed to be the increase in proportion of sp^2-bonded grain boundaries in finer grain nano-diamond films. The best electron field emission properties attainable is J_e = 500 μA/cm^2 at 20 V/μm and E_0 = 8.5 V/μm.

關鍵字： 奈米微晶鑽石、偏壓孕核、電子場發射特性
Nano-diamond, BEN, BEG, Electron field emission

一、研究背景：

Diamond and related materials grown have enormous potential applications due to their marvelous physical and chemical properties[1-3]. Diamond films also possess negative electron field emission properties and are of great potential for the applications as electron sources[4]. Another good candidate, carbon nanotube, own superior electron field emission properties to the diamond films, but involves catalysts in the synthesis process and has poor processing reliability. Therefore, there have wide interest in how to improve the electron field emission properties of diamond films recently. One of the possible routes for increasing the electron field emission capacity of diamond films is to increase the proportion of grain boundary region, as it has been proposed that the grain boundaries contain sp^2-bond[5] and provide conduction path for electron, facilitating the electron field emission process.

Increasing nucleation density is of critical importance for the purpose of synthesizing nano-diamonds. Various techniques, such as seeding with diamond particulates[6], surface scratching[7], ion implantation[8], and laser pre-processing[9], have been applied to enhance the nucleation rate for growing diamond films. Bias enhanced nucleation (BEN) process is overwhelmingly advantageous to these pre-nucleation processes[10-12] and can achieve a very high nucleation density. Recently, Sharda et.al.[13] and Jiang et.al.[14] extended the bias voltage over growing period, which markedly enhanced the secondary nucleation and lead to the growth of nano-diamond films.

In this paper, we adopted the bias enhanced technique for promoting the nucleation of nano-diamonds and suppressing the growth of grains. The effect of growth parameter on the microstructure and crystal structure of the nano-diamond films were systematically studies. These characteristics were than correlated with the electron field emission properties of the films. A possible mechanism was discussed.

二、研究方法：

The diamond films were grown in a 2.45 GHz ASTeX microwave plasma enhanced chemical vapor deposition (PECVD) system on

P-type mirror polished Si (100) substrates. No diamond powder or any other ex situ treatment was performed prior to the depositions. The substrate assembly was immersed in methane and hydrogen plasma. The depositions were carried out under continuous negative dc bias from 75 to 175 V to the substrate. While the bias voltage was held constant throughout the deposition, bias current varied with time in the same fashion as commonly observed in biased enhanced nucleation in the growth of CVD diamond; the current increases after some incubation period followed by saturation at longer deposition time. The increase in the current is attributed to enhancement in electron emission from the surface as highly emissive diamond is deposited on silicon. The sets of depositions were carried out at various methane concentrations in balance hydrogen, and biasing voltages at a pressure of 55 Torr, with a microwave power of 1500 W. The films were characterized using Raman spectroscopy and field emission scanning electron microscopy (FESEM). Micro-Raman measurements were performed at room temperature, using 514.5 nm laser as the excitation source. Electron field emission from diamond films were measured using computer controlled Keithley (Model 237) high voltage supply.

三、研究結果與討論

In microwave plasma enhanced CVD growing process, the CH_4/H_2 ratio and bias voltage are observed to influence the nucleation behavior and the characteristics of nano-diamond films most prominently. Figure 1(a) shows general behavior for the time evolution of bias current during nucleation stage. It is observed that, under -150 V bias voltage and CH_4/H_2=3% gas mixture, the bias current increases abruptly at around 60 min (curve I), indicating the onset of nano-diamond nuclei formation. This figure reveals that increasing the methane content in the gas mixture markedly shorten the onset time interval for the formation of nuclei, viz. it enhances the nucleation rate for the nano-diamonds, which is apparently due to increase carbon species in the reacting gases.

Typical microstructure of the nano-diamond films grown under the same conditions are shown in Fig. 2(a), which illustrates that the grains are very small, ~ 32 nm, and are distributed uniformly. Cross-sectional micrograph shown as inset in Fig. 2(a) indicates that the films thickness is very uniform. The average grain size of the nano-diamond films varies insignificantly with the CH_4/H_2 ratio in the reaction chamber, as shown in Fig. 2(b) (solid squares). Raman spectra of these films are very alike (Fig. 3(a)), that is , all of them show very diffuse resonance peak in the vicinity of 1150 cm^{-1} (D^*), 1332 cm^{-1} (D) and 1580 cm^{-1} (G), which is similar to the Raman spectra for nano-diamond reported in the literatures.

While the CH_4/H_2 ratio in reaction chamber imposes insignificant influence on the SEM granular structure and Raman resonance characteristics of the nano-diamond films, it does show marked effect on the electron field emission properties of the films. Figure 4(a) indicates that the electron field emission for the nano-diamond films can be turned on at around 10 V/ m and the maximum electron field emission current density varies with the CH_4/H_2 ratio in the deposition chamber, showing largest J_e-value for CH_4/H_2 = 5% case, viz. J_e = 400 μA/cm^2 at 20 V/ m applied field. Too high CH_4/H_2 ratio markedly degrades the electron field emission properties, which is probably due to the increasing sp^2-content in the films. However, Raman spectroscopy can not clearly resolve such a characteristic and more detailed investigation is needed.

To further improves the electron field emission properties of the films, bias voltage at nucleation and growth stage of NCD process was systematically varied. Figure 1(b) indicates that , for CH_4/H_2 = 5% case, the bias current increases abruptly at around 30 min indicating the onset of forming nano-diamond nuclei, the bias current saturates at about 40 min after biasing (-100 V), which indicates fully coverage of nano-diamond nuclei. The incubation time, the time interval for the formation of nano-diamond nuclei, increases with the applied bias voltage. In -175 V biased situation, it takes more than 105 min to start the formation of nano-diamond nuclei. But they cover the surface in a very short time interval after the onset of nuclei formation. While the increases in nucleation rate with CH_4/H_2 is understandable, the mechanism for the retardation of nano-diamond nuclei formation due to larger applied bias is not as obvious. The bias voltage not only increases the kinetic energy for the C^+-species, which is expected to enhance the formation of sp^3-bonds, but also raises the bombardment energy of H^+-species, which will increase the etching efficient for the freshly formed C-C bonds. The results shown in Fig. 1(b) implies apparently that H^+ etching effect predominate the process.

The microstructure of these nano-diamond

films is similar to the one shown in Fig. 2(a). Contrary to the phenomenon that CH_4/H_2 ratio essentially shows no influence in grain size of the nano-diamond films, the bias voltage markedly alters the grain size pronouncedly, this is, the larger the bias voltage is, the smaller the grains (Fig. 2(b), solid circles). Moreover, too large bias voltage (>-175 V) not only suppresses the growth of the nano-diamond gains, but also induces the formation of aggregates, as shown in Fig.2(c) for -175 V bias grown films. Presumably, the aggregates are resulted bombardment etching by energetic H^+-species, which is in accord with the bias effect on retarding the nucleation of diamond. In contract, too low bias voltage (<-75 V) can not effectively suppress the growth of diamond grains, such that a duplex granular structure in resulted (not shown). Raman spectroscopy again, can not resolve the difference in structure of the films. As illustrated in Fig. 3(b) all the Raman spectra contain broaden resonance peaks in the vicinity of D^*, D and G-band position. There is no clear resonance peak at 1480 cm^{-1}, the commonly reported one for nano-diamonds. Bias voltage modifies the electron field emission properties of the nano-diamond films ever more significantly than the CH_4/H_2 ratio does. Figure 4(b) shows that higher bias voltage results in larger electron field emission current density.

Above mentioned results indicate that although the SEM granular structure and Raman crystal structure of these nano-diamonds are very alike, the processing parameters, CH_4/H_2-ratio and bias-voltage, does impose markedly influence on the electron field emission characteristics of the films. It should be noted that all the nano-diamond films posses low resistively (~ 10^2 ·cm). Such that the electron transport characteristic can not be the prime factor altering the electron field emission behavior of the nano-diamond films. Comparing the Fig. 2(b) and Fig. 4(b) reveals an interesting phenomenon, viz. the nano-diamond films possessing superior electron field emission properties, which were synthesized under large bias voltage (-150 & -175 V), are of smaller grain size (~20 nm). In contract, those grown under smaller bias voltage (-75 ~ -125 V) show inferior electron field emission behavior and are of larger grain size (~55 nm). This phenomenon implies that larger proportion of grain boundaries for the finer grain size materials is possibly the main cause, resulting in better electron field emission properties. Such an assumption is in accord with the proposed structure for the nano-diamonds, viz. the grain boundaries of nano-diamonds are sp^2-bounded and the grains are sp^3-bonded. The sp^2-bonded regions are low resistivity and act as electron transport path, which facilitates the electron field emission properties.

四、結論：

The morphologies and field emission properties of these diamond films are observed to be strongly correlated with the deposition conditions, such as CH_4/H_2 ratio and bias voltage. Effects of CH_4/H_2 ratio and bias voltage on the nucleation behavior and the characteristics of the nano-diamonds were investigated. Among the two major factors, the bias-voltage shows more prominent effect on modifying the nucleation rate for diamond nuclei and granular structure for the nano-diamonds. While the SEM microstructure and Raman crystal structure of the films insignificantly vary, the electron field emission properties of the materials markedly change, with these deposition parameters. The main factor modifying the electron field emission properties is assumed to be the increase in proportion of sp^2-bonded grain boundaries in finer grain nano-diamond films. The best electron field emission properties attainable is J_e = 500 μA/cm^2 at 20 V/μm and E_0 = 8.5 V/μm, which is larger than that of large grain ones.

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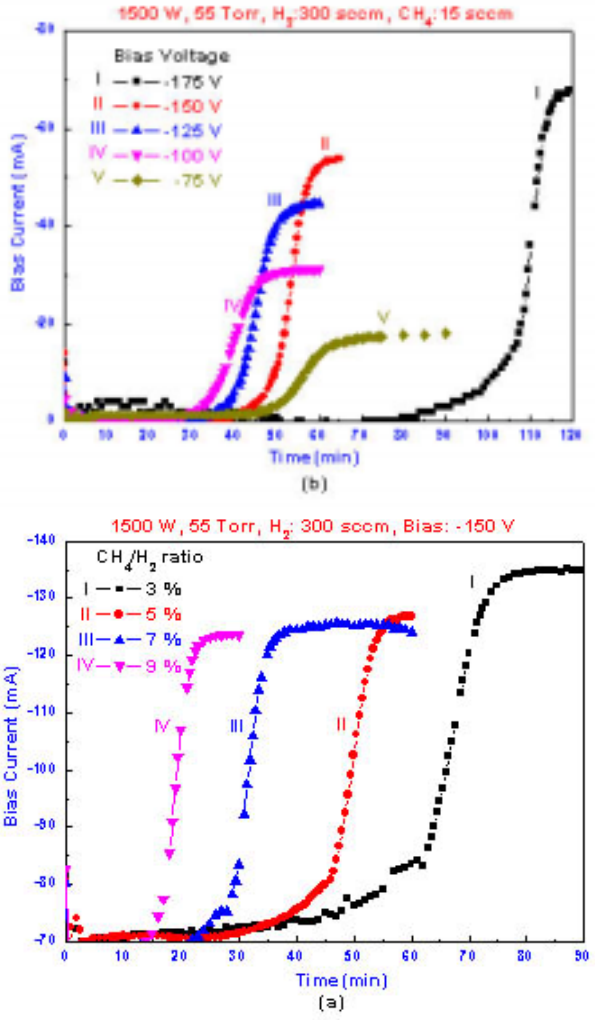

Fig. 1 Variation of bias current-time characteristics during nucleation stage in MPE-CVD process: (a) CH_4/H_2 = 3~9 % with -150 bias voltage and (b) bias voltage = -75~-175 V with CH_4/H_2 = 5 % (H_2 = 300 sccm and total pressure is 55 Torr).

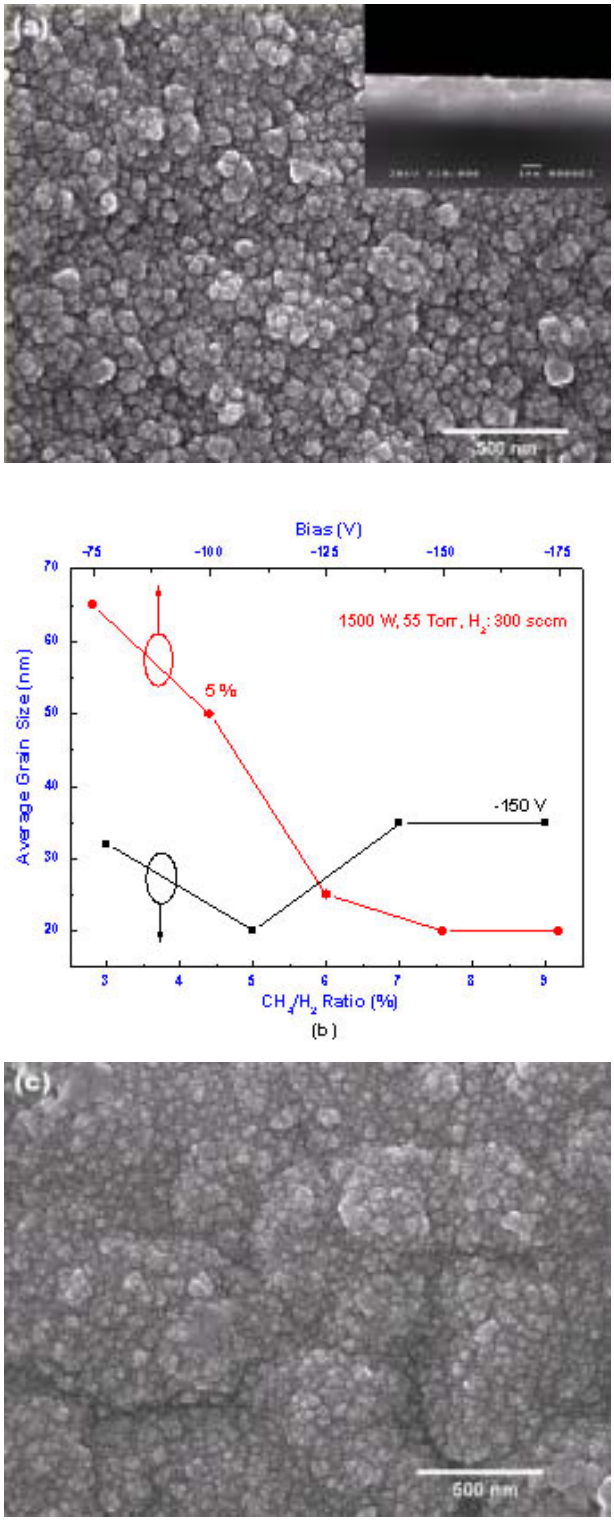

Fig. 2 (a) Typical SEM micrograph of nano-diamonds grown under -150 bias voltage (H_2 = 300 sccm) with the inset showing the cross-section micrograph of the films, (b) variation of grain size with CH_4/H_2-ratio and (c) SEM micrograph of nano-diamonds grown under -175 V bias voltage (total pressure 55 Torr, CH_4/H_2 = 5 %, H_2 = 300 sccm).

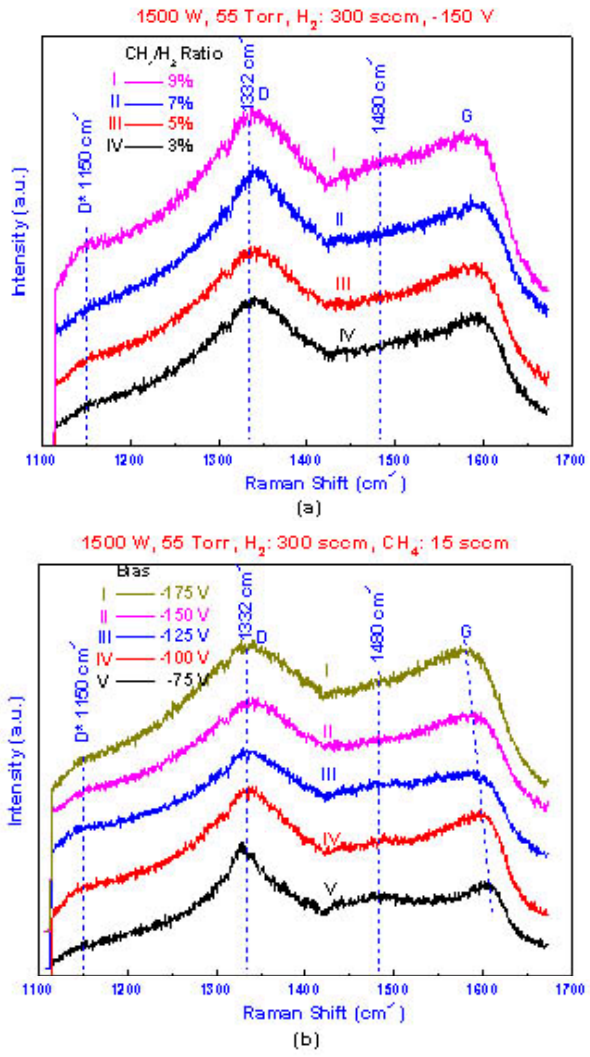

Fig. 3 Raman spectra of nano-diamond films deposited under (a) -150 V bias voltage with CH_4/H_2 = 3~9 %, and (b) under CH_4/H_2 = 5 % with -75~-175 V bias voltage (H_2 = 300 sccm and total pressure is 55 Torr).

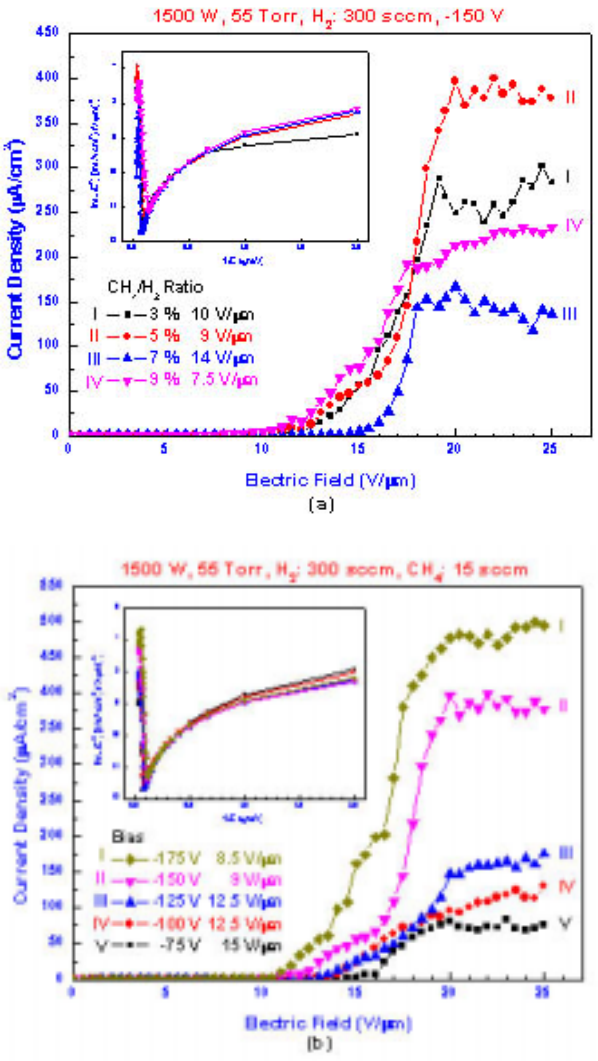

Fig. 4 Electron field emission properties of nano-diamonds, deposited under (a) -150 V bias voltage with CH_4/H_2 = 3~9 %, and (b) under CH_4/H_2 = 5 % with -75~-175 V bias voltage (H_2 = 300 sccm and total pressure is 55 Torr).